N 63 21361

Technical Report No. 32-425

The Development of the Surveyor Gas Chromatograph

W. F. Wilhite

jpl

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

May 15, 1963

OTS PRICE

XEROX $ 1.60

MICROFILM $ 0.80

Technical Report No. 32-425

The Development of the Surveyor Gas Chromatograph

W. F. Wilhite

Karl W. Linnes

Karl W. Linnes, Chief
Space Instrument Systems Section

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

May 15, 1963

Copyright © 1963
Jet Propulsion Laboratory
California Institute of Technology

Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

CONTENTS

TABLES

FIGURES

ACKNOWLEDGMENTS

The author wishes to thank V. I. Oyama, Jet Propulsion Laboratory; Dr. S. R. Lipsky, Yale University; and Dr. J. E. Lovelock, Baylor University, for their valuable assistance in the development of the *Surveyor* gas chromatograph.

ABSTRACT

This Report discusses the development of a gas chromatograph constructed for the Jet Propulsion Laboratory by Beckman Instruments, Incorporated. The instrument is designed to be soft-landed on the surface of the Moon as part of the *Surveyor* scientific payload. While on the lunar surface, the gas chromatograph should provide an analysis of the volatile constituents in a sample of the lunar surface material. The Report discusses provisions for thermal control of the operating instrument over a wide range of ambient temperatures; packaging necessary to meet the severe vibration and temperature environments; and problems encountered in the design of subassemblies of the instrument, such as solid sample handling and heating in the oven subassembly, programmed valving, column materials, sample detection, signal processing, and calibration.

I. INTRODUCTION

A gas chromatograph has been designed to be used as part of the *Surveyor* scientific mission, in order to provide an analysis of the volatile constituents in the lunar crust material. Information thus obtained may indicate the state of organic chemical equilibrium that exists on the Moon and the relative distribution of certain organic compounds on the lunar surface. Such data may provide clues not only to the possibility of present or past life on the Moon, but also to the origin of life on the Earth (Ref. 1).

When the chromatograph is in operation, samples of the lunar crust will be collected by the appropriate sampling devices on the *Surveyor* spacecraft and delivered to the chromatograph for analysis. The delivered samples

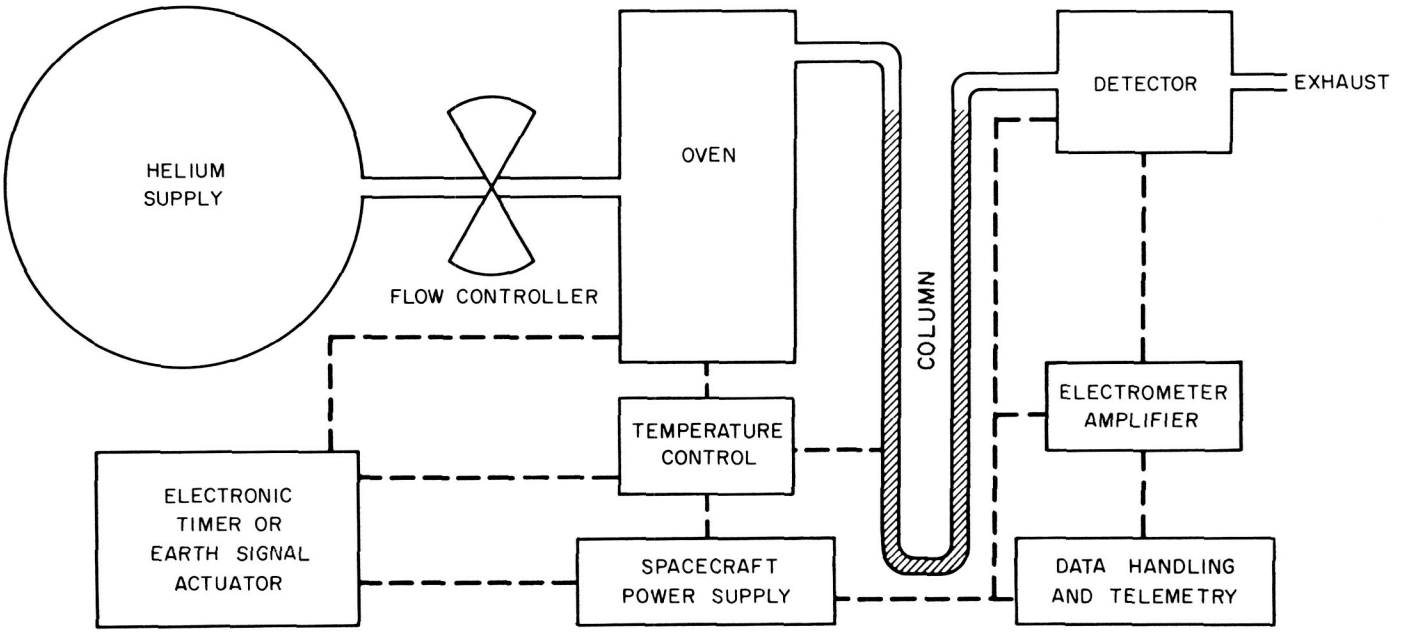

Fig. 1. Schematic drawing of the *Surveyor* gas chromatograph

will pass through a funnel in the top of the chromatograph into a small oven. The oven will then be sealed and will be heated to release any gaseous material that is present in the sample. The gases thus liberated will be injected into a helium carrier-gas stream in the form of a tight slug. The sample gas will then be divided and swept through analytical packed columns. The constituents of the sample gas will have more or less affinity for the packing material in the columns. Through the mechanisms of adsorption and/or chemical equilibrium, the passage of each constituent through the columns will be impeded for a distinct, reproducible time interval unique for each unknown. This retention time will be measured by a signal from a detector at the effluent end of each column; the detectors sense the presence of any material other than the helium carrier-gas. The outputs from the detectors will be fed into the spacecraft for data processing and transmission back to Earth. From these transmitted data, the identity and the approximate quantity of each volatile constituent in the sample will be determined. Figure 1 is a schematic drawing of the foregoing operation.

A prototype model (P-2) of the gas chromatograph (Fig. 2), designed to meet the environmental restraints placed on *Surveyor* instruments, was built by Beckman

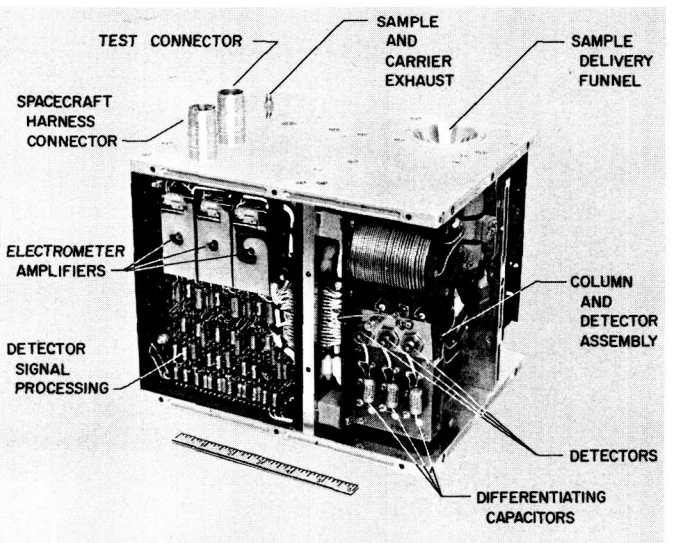

Fig. 2. *Surveyor* gas chromatograph prototype model P-2

Instruments, Incorporated, and was delivered to the Jet Propulsion Laboratory (JPL) on December 8, 1962. The instrument weighs 14 lb and has a volume displacement of 640 in^3. The total operating energy required per 100-min analysis is 24 w-hr.

II. PERFORMANCE OF THE GAS CHROMATOGRAPH PROTOTYPE MODEL P-2

Stringent performance and environmental requirements were established for the chromatograph in order that the instrument could be expected to fulfill its mission in the lunar environment. The design and functional specifications for the chromatograph are given in Ref. 2 and 3 and are summarized in Tables 1 and 2.

Prior to the delivery of the prototype model P-2 of the chromatograph, an acceptance test was performed on this instrument at Beckman Instruments, Incorporated. The chromatograph met or exceeded all the requirements, with a few exceptions. The over-all test results are discussed below.

The specifications required the chromatograph to resolve 28 specific components ranging in molecular weight from hydrogen to butyric acid, as shown in Table 1. These components were chosen so that the gas chromatograph would have a particular resolution capability consistent with its lunar mission.

The chromatograph satisfactorily resolved all of the 28 components except formaldehyde, acetonitrile, hydrogen cyanide, carbon dioxide, hydrogen sulfide, and butyric acid. It is felt that the resolution of these components can readily be accomplished with additional column development work on the chromatograph.

The instrument was required to have the sensitivity to detect a quantity at least as small as 3×10^{-10} mole for each of the 28 components. This requirement was met for all the components resolved, with the exception of ethane. The requirement can probably be met with some adjustment in the flow of the molecular sieve column (see Section III-B below).

The reliability of the detector signal processor was tested under difficult environmental conditions, including temperature ranges expected to be encountered in lunar missions. The equipment was demonstrated to have the required linearity, dynamic range, output level, and constancy of gain and zero over the actual operating temperature range of -30 to $+100$°C.

The various pneumatic fittings and valves were required to have leakages of less than 10^{-3} or 10^{-4} cm³/sec, depending on their location. During the acceptance tests, it was demonstrated that most of the leakages of helium within the instrument were less than 10^{-6} cm³/sec.

Table 1. Performance requirements for the gas chromatograph

Components resolved:	Hydrogen	Propionaldehyde
	Oxygen	Formic acid
	Nitrogen	Acetic acid
	Carbon monoxide	Butyric acid
	Carbon dioxide	Benzene
	Methane	Toluene
	Ethane	Acetone
	Propane	Acetonitrile
	Butane	Acetylene
	Methanol	Acrolein
	Ethanol	Hydrogen cyanide
	Propanol	Hydrogen sulfide
	Formaldehyde	Ammonia
	Acetaldehyde	Water
Maximum retention time, min		30
Minimum detectable quantity in oven, mole		3×10^{-10}
Minimum dynamic range of detection		10,000 times minimum detectable quantity
Oven temperature control, °C		±10
Oven maximum heating time, min		4
Detector and signal processing		
Output, v		0 to 5
Maximum noise level (peak to peak), mv		100
Minimum detectable signal twice the maximum noise level		
Accuracy, %		±1
High and low sensitivity read out simultaneously		
Oven seal maximum leakage (helium), cm³/sec		10^{-6}
Column temperature control, °C		±0.25
Valves maximum leakage (helium), cm³/sec		10^{-4}
Retention time reproducibility, %		1
Pressure regulation, %		1
Calibration sample reproducibility, %		4

Table 2. Environmental requirements for the gas chromatograph

Item	Value
Sterilization	
Heat	125°C (257°F) for 36 hr
Ethylene oxide	24 hr
Vibration	42 g peak-to-peak over frequency range of 20 to 1,500 cps
Shock	35 g for 5 msec
Ambient survival temperature range	−185 to +125°C (−301 to +257°F)
Ambient operating temperature range	−50 to + 125°C (−58 to +257°F)

As part of the acceptance test, a continuous 35-hr run was made in a vacuum compartment at a pressure of 10^{-5} mm Hg. Twenty-one consecutive analyses were performed during this period, using gaseous samples from the standard sample container. The data were read out continuously on six potentiometric recorders. Various parameters, such as input power supply voltages, were changed within specified tolerances, and temperatures were measured during the course of the 21 analyses. Gaseous samples were processed in the oven at three different oven temperatures, and each sample was introduced into the instrument at the start or near the end of the oven heating cycle to ascertain whether the oven seal deteriorated in the course of the analyses. Most of the functional specifications of the instrument were effectively demonstrated during this 35-hr run.

III. SUBASSEMBLY DEVELOPMENT HISTORY

The gas chromatograph consists of the following subassemblies or systems:

1. The oven assembly (Fig. 3 and 4), which accepts the delivered sample and heats the solid material, driving off the volatile constituents.
2. The column and detector assembly (Fig. 2 and 4), which is the heart of the instrument, and consists of three parallel columns with a detector at the effluent end of each column.
3. The detector signal processing circuitry, temperature control circuitry, and other associated electronic equipment (Fig. 2 and 4).
4. The pneumatic components, which consist of the helium carrier-gas container (Fig. 3), the helium pressure regulator and solenoid valve (Fig. 3), and the standard sample container (Fig. 4).
5. The programming valve (Fig. 4), which performs and coordinates the programmed pneumatic and electrical functions necessary for the operation of the chromatograph.

This Part describes briefly the development history of each subassembly, showing some of the outstanding problems encountered.

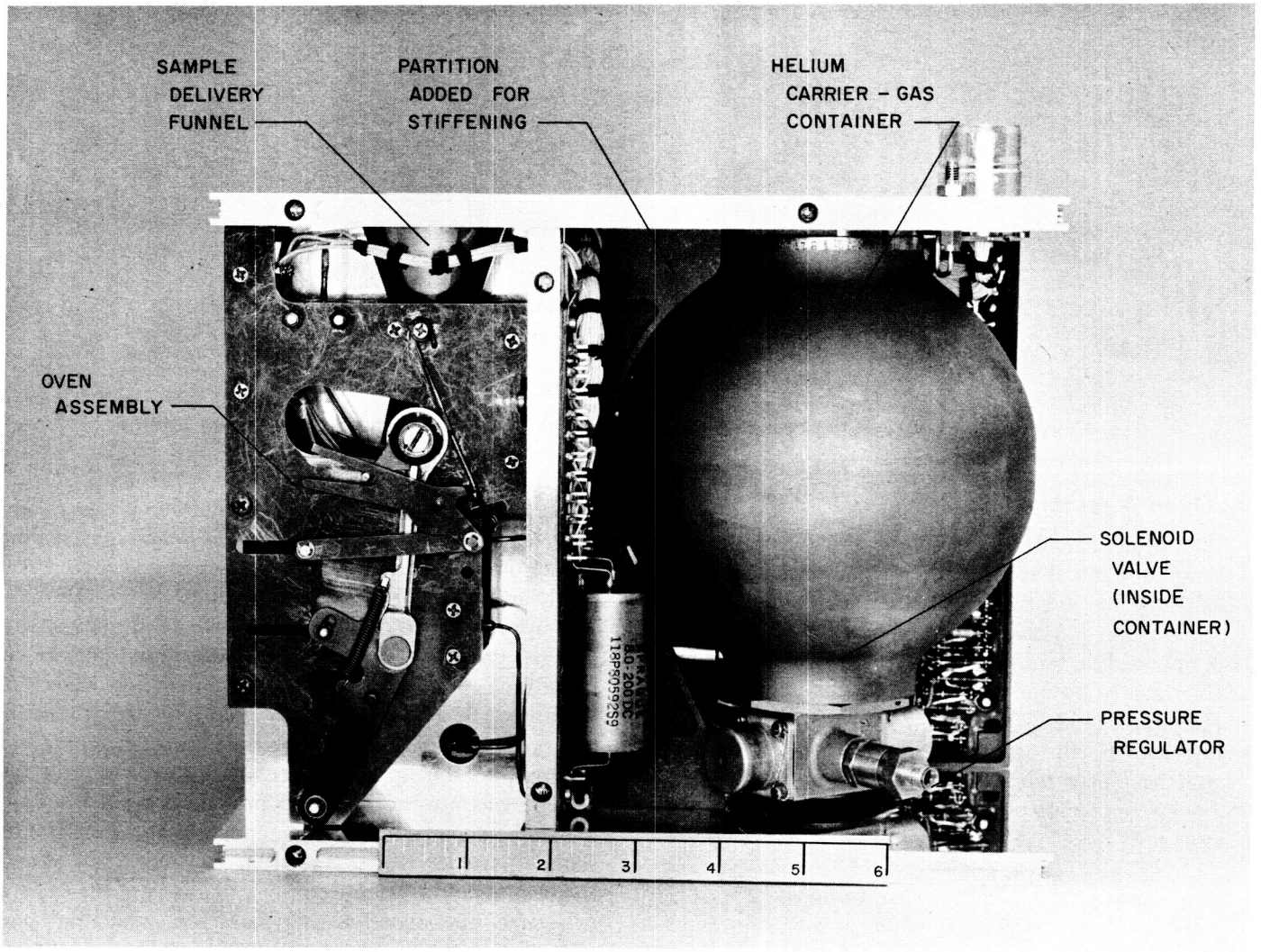

Fig. 3. View of gas chromatograph showing oven assembly and helium container

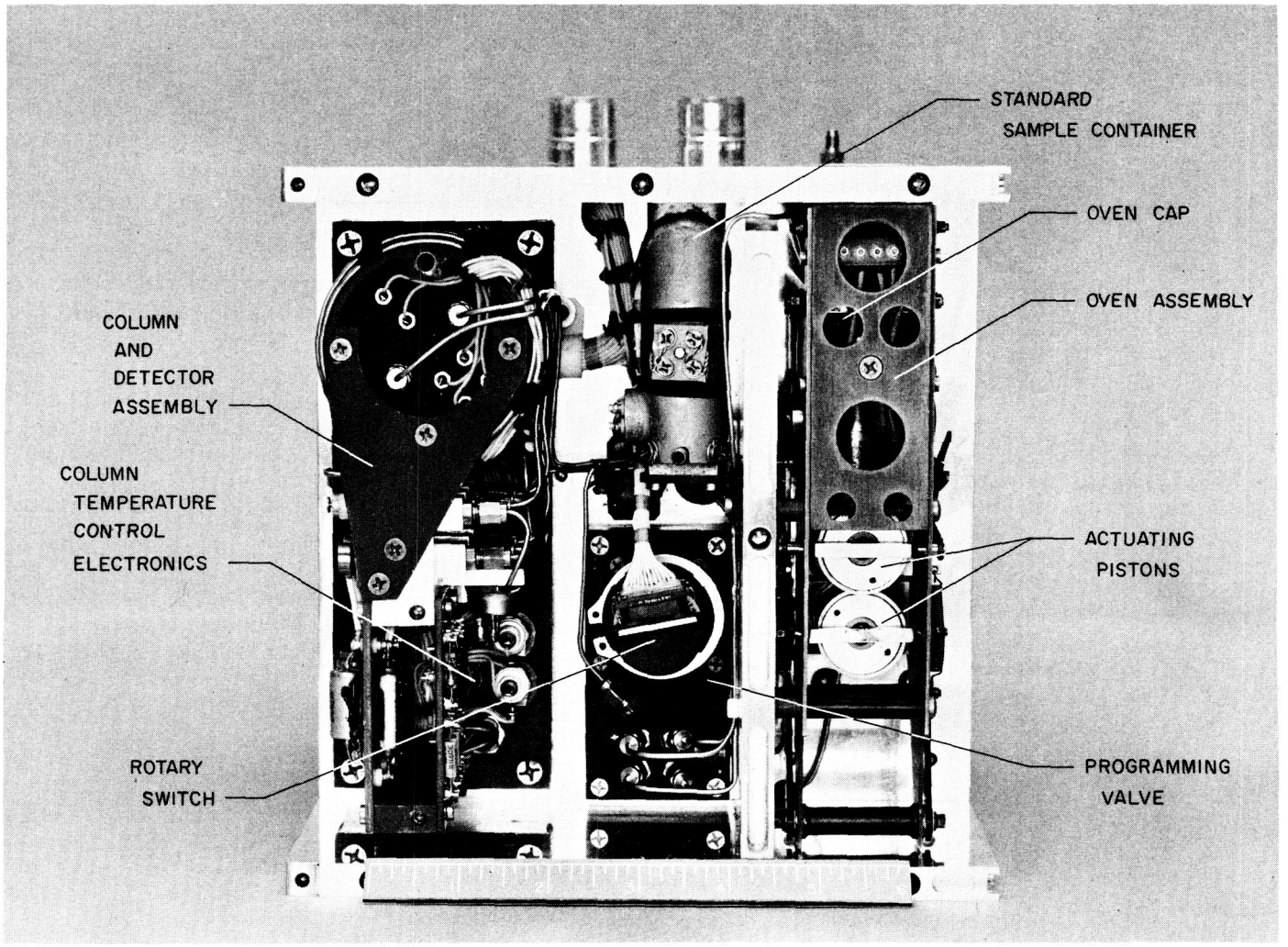

Fig. 4. View of gas chromatograph showing programming valve and standard sample container

A. Oven Assembly

The oven assembly consists of the oven, the oven sealing cap, and the pneumatic actuators that move the oven. After the oven accepts a sample of lunar material with a volume of 3 ± 1 cm^3, it is moved under the sealing cap, thus sealing the sample within the oven. The sample is then heated to one of three proportionally controlled temperatures (150, 325, or 500°C) to be selected on command from Earth. After the volatile constituents of the sample have been released and injected into the columns, the oven is pneumatically actuated to dump the spent sample.

The oven seal is required not to have a leak rate greater than 10^{-6} cm^3/sec of helium, which represents a loss of 0.01% of sample during the oven heating cycle. For obvious reasons, no organic materials can be exposed to the sample within the oven, which means that the oven seal must be metal-to-metal. Numerous sealing techniques were evaluated before a modified K-ring seal finally evolved. This seal is built into the sealing cap. The upper surface of the oven, which seals against this cap, is ground optically flat. This upper surface is made from Stellite, which has a Rockwell hardness of 60 to 62. The K-ring is heavily gold-plated to eliminate any possibility of cold-welding (owing to the high lunar vacuum) to the upper surface of the oven during the seal. It was also necessary to provide a small brush of glass fibers embedded in an epoxy resin, so that any sample particles which landed on the sealing surface of the oven would be removed prior to allowing the surface to contact the plated K-ring seal. This technique provides an open seal which meets the low-leak-rate requirement for over 100 consecutive sealings.

The mechanisms for moving the oven into the different positions of accepting the delivered sample, sealing, and dumping the spent sample are actuated by double O-ring pneumatic pistons (Fig. 4) which are pressured from the helium carrier-gas cylinder. Many problems were encountered in designing the complex oven-moving mechanism so that the structural strength would be sufficient to withstand the severe *Surveyor* vibration environment. All of these problem areas appear to be solved, as evidenced by environmental development tests that have been run on the gas chromatograph (see Part V).

B. Column and Detector Assembly

The three parallel columns in the chromatograph are: a 7-ft molecular-sieve 5A column to separate the fixed gases; a 15-ft column with Carbowax 1540 on T-6 Teflon-particle support to separate water and most of the hydrocarbons; and a 12-ft column with Apiezon L, Carbowax 20M, and phosphoric acid on a Chromosorb support to separate the organic acids. These columns are wound on the outside of a threaded magnesium mandrel, together with a heater and a temperature sensor element (Fig. 2). A 7½-ft. length of tubing to provide the correct sample volume is wound on the inside of this mandrel.

The temperature of the entire column package is controlled at 105°C. The electronic equipment associated with the column temperature controller is mounted with the column package (Fig. 4). Heat dissipated by the controller is used to partially heat the column and detector. This system provides full proportional temperature control and maintains the column temperature within 0.1°C. The detector block is maintained 1 to 3 °C higher than the column so that no condensation of components takes place in the detectors. The assembly, which is covered with a superinsulation-wrapped box to reduce loss of heat by radiation, is mounted structurally to the package by insulating mounting blocks.

The three detectors (Fig. 2) used in this chromatograph are glow-discharge-type devices and act electrically similar to a gas-filled voltage-regulator tube. Figure 5 shows a typical detector signal. Under a fixed set of conditions with a specific carrier gas, in this case helium, the detector has a specific breakdown voltage V_d. Introducing a contaminant gas, in this case a sample component, to the carrier causes a change, u_p, in the breakdown voltage. When the contaminant has passed, the breakdown voltage returns to its original value. These peaks of voltage as a function of time contain the information necessary to identify the amount and type of the sample component in the carrier.

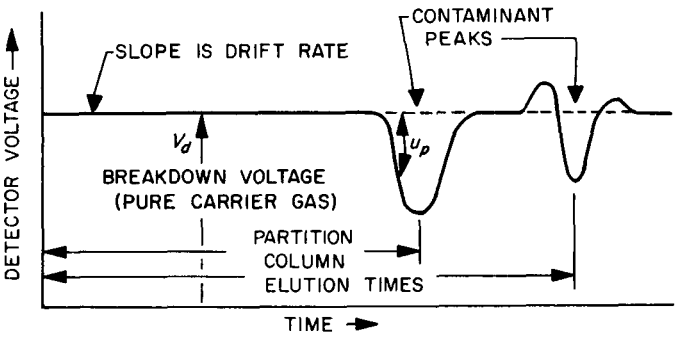

Fig. 5. Typical detector signal

One of the main problems in the use of this detector was that of zeroing the detector in the absence of a sample. Many automatic servo-type systems were discussed and discarded. It was finally decided to use a derivative readout of the chromatographic peaks, thereby eliminating the effect of dc drift associated with the breakdown voltage of the detector. The derivative was obtained simply by coupling the detector to the electrometer amplifier through a capacitor (Fig. 2). An advantageous side effect of the derivative of the chromatogram is that the retention time of a peak (which identifies the component) can be accurately determined, as seen in Fig. 6.

C. Detector-Signal Processing Circuitry

The detector-signal processing circuitry consists mainly of three chopper-stabilized electrometer amplifiers. A block diagram of these amplifiers is shown in Fig. 7. The requirements imposed on these amplifiers are shown in Table 1. During the acceptance tests, the amplifiers successfully demonstrated compliance with these specifications.

As shown in Table 1, two ranges of sensitivity are read out of the amplifiers simultaneously. The high-sensitivity output is 100 times the amplification of the low-sensitivity output. A large input signal can drive the high-sensitivity amplifier beyond operating limits; however, this condition reflects no distortion into the low-sensitivity output. Under these circumstances, the low-sensitivity output contains a discernible signal and no information is lost. This dual output arrangement covers the dynamic range of 10,000, with each output covering a range of 100.

D. Pneumatic Subsystem

The pneumatic subsystem of the gas chromatograph consists of the helium carrier-gas container, the helium

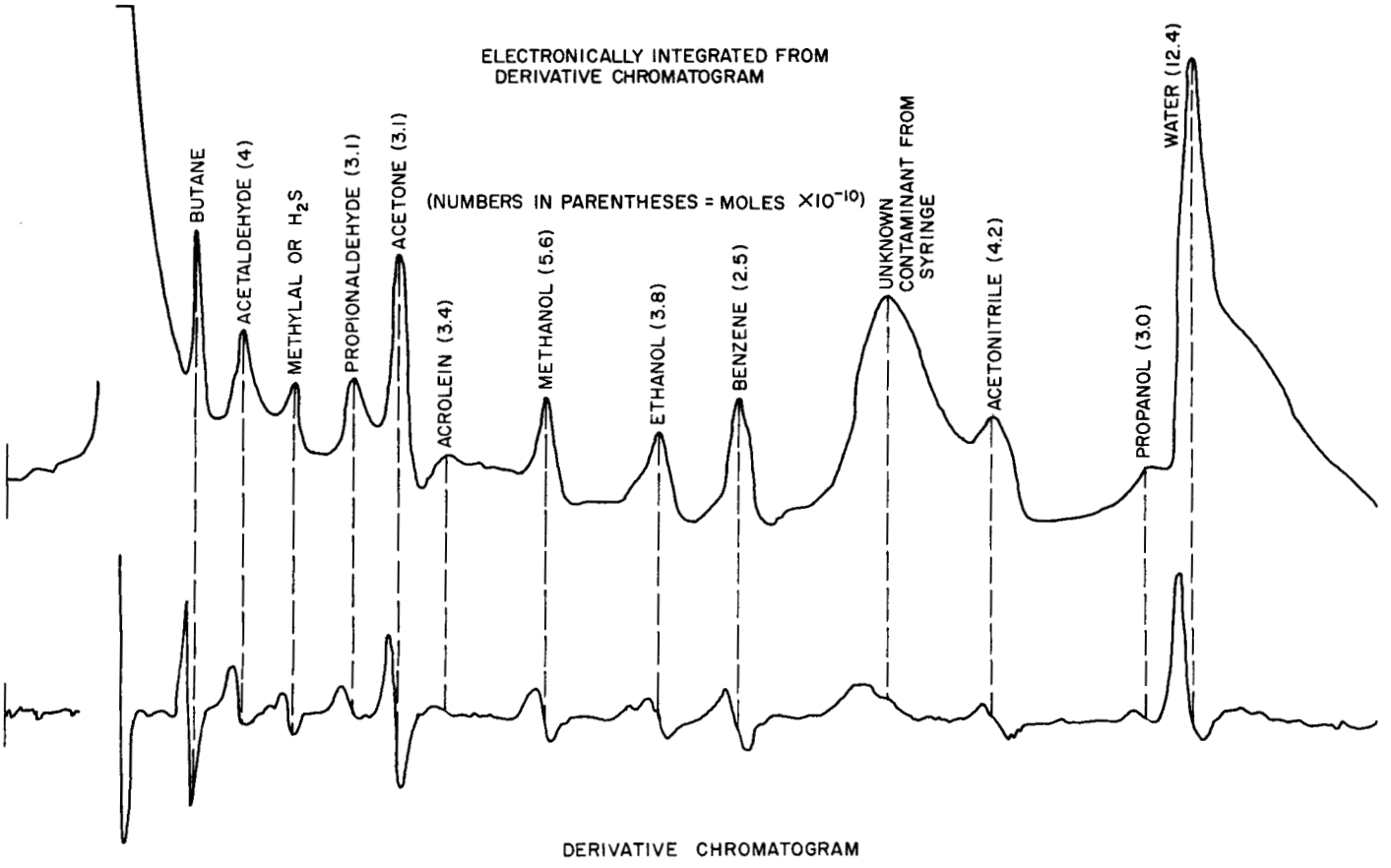

Fig. 6. Derivative readout chromatogram

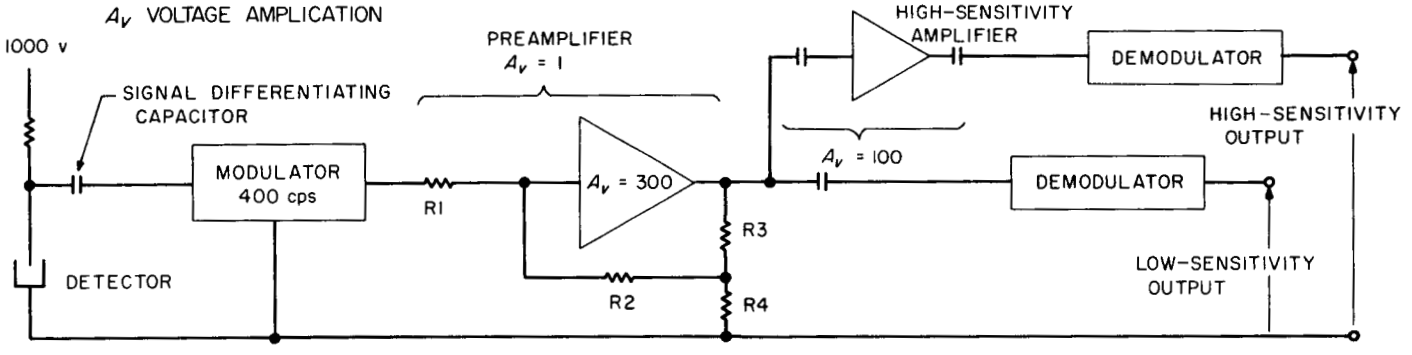

Fig. 7. Schematic drawing of electrometer amplifier

solenoid valve, the pressure regulator, and the standard sample container and valving.

1. Helium Container

The helium carrier-gas container (Fig. 3) is a titanium sphere designed in such a way that it is mounted between the top and bottom panels of the instrument, serving as a rigid beam between these two structural members. The cylinder was designed to a bursting pressure of 10,000 psi with an 8,000-psi test strength and a 6,000-psi working strength. In use, the cylinder is loaded to 2,200 psi at 25°C. This provides sufficient helium as carrier gas and as pneumatic operating gas for approximately 70 hr, or double the time that is required to complete the lunar mission.

2. Pressure Regulator and Helium Solenoid Valve

The pressure regulator (Fig. 3) is a 2-stage regulator with the first stage regulating to 200 psi and the second stage adjustable from 40 to 80 psi. The regulator is completely temperature-compensated. The solenoid valve, which is used to shut off the helium supply until it is needed, is of a latching type so that no power is required to keep the valve in either the open or the closed position. To save space, the solenoid valve itself is mounted within the helium container and uses the 2-stage pressure regulator as an integral part of the valve.

3. Standard Sample Container

The standard sample container (Fig. 5) provides a means of calibrating the gas chromatograph after it has landed on the lunar surface. This device consists of a small container for the standard sample, together with two solenoid valves which, when properly actuated, inject a reproducible volume of the standard sample into the carrier gas for calibration purposes. The container has a volume of approximately 2 in^3 and can be loaded to 100 psi. The sample volume delivered in each "shot" is approximately 0.15 cm^3.

E. Programming Valve

The programming valve performs and coordinates the programmed pneumatic and electrical functions of the chromatograph. This is accomplished by a motor-driven idler gear which drives a geared pneumatic valve and a geared rotary switch (Fig. 4). The pneumatic valve consists of an optically flat, drilled rotor with Viton A O-rings running against it for seals. Holes are drilled through the rotor so that different hole positions on each side of the rotor are connected in various ways. This allows different pneumatic lines on either side of the rotor to be aligned at the proper time so that pneumatic functions are carried out.

The most critical part of the valve consists of the O-rings, which must meet the leakage requirements over several hundred cycles and over the entire operating temperature range of -50 to $+100°C$. The O-rings must also be capable of being frozen in a static position during the lunar night and, on reaching operating temperature the second lunar day, must regain the required resiliency to provide a satisfactory seal. They must also withstand the hard lunar vacuum without deterioration. Viton A is the best O-ring material that has been found to date.

IV. THERMAL ANALYSIS OF THE GAS CHROMATOGRAPH

One of the most difficult problems in the over-all design of the *Surveyor* gas chromatograph is the maintenance of proper thermodynamic conditions under the extreme environmental constraints.

The thermal design of the gas chromatograph package was developed around the concept of an uninsulated isothermal system whose equilibrium temperature was below the column subassembly operating temperature. The feasibility of this design approach was established in the early design states by an estimate of the average operating temperature of the gas chromatograph package at lunar noon. It was decided at that time to maintain the lunar noon operating temperature at the lowest temperatures possible to provide a sufficient margin of safety. This is accomplished by painting three external surfaces with a white inorganic paint developed by the Hughes Aircraft Company. The three sides thus painted are the top, the outboard side, and the adjacent inboard side that faces the X-ray diffractometer. The other three faces are of polished aluminum. With the passive temperature control thus provided, the maximum temperature of the gas chromatograph package, excluding the column subassembly and the region near the oven, will be 72°C at lunar noon. The minimum temperature that the gas chromatograph package will experience during the coldest part of the lunar night is estimated to be −182°C.

The column package and the oven compartment were thermally designed according to specific rules that were determined by functional requirements and power limitations. The design rules specified limits in the trasient and steady stages. It was shown during the acceptance tests that all of the requirements in this area were met.

Using 30 w of heating power, the column package was heated from −50°C to the operating temperature of +105°C in 35 min. The maximum temperature difference on the column coil assembly did not exceed 1°C, and the detector block temperature was always 1 to 3°C higher than the column coil assembly in the steady-state condition.

With 40 w of heating power, the oven was heated from −50 to +500°C in 3.2 min (Fig. 8). The oven holding power at 500°C was 10 w. The oven subassembly is a complex system of moving mechanical and structural components that is designed to perform in a broad temperature range and stand severe shock and vibrational

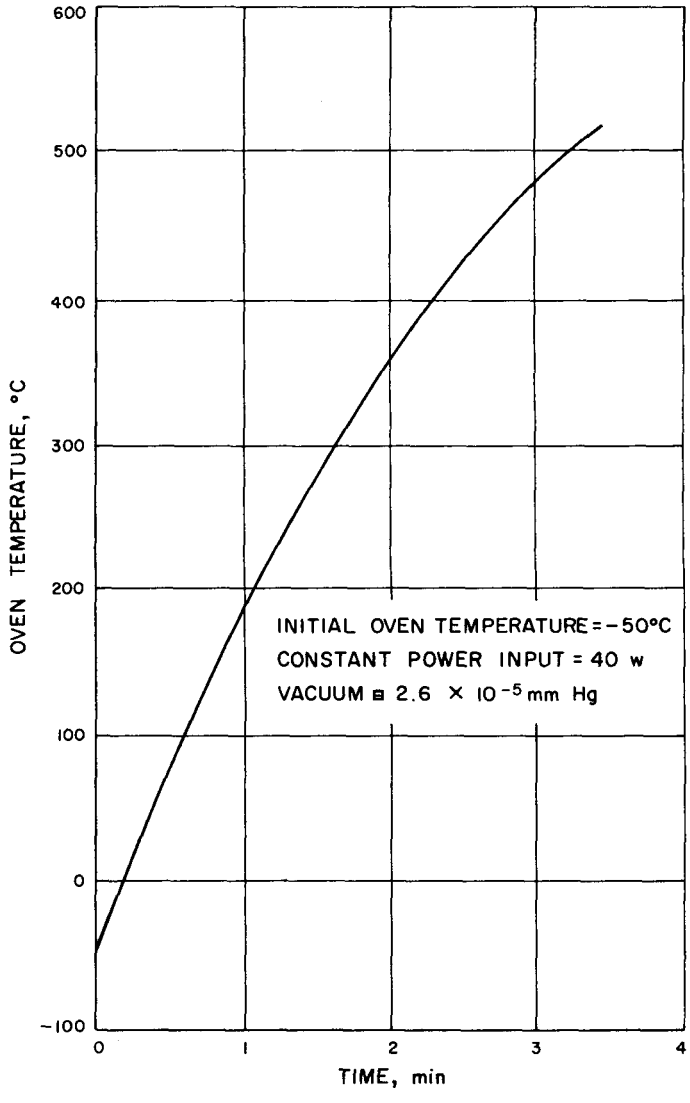

Fig. 8. Results of oven heating-rate test

load at takeoff and touchdown. A structure that is designed to withstand severe loads is invariably a relatively good conductor of heat. This type of structural design opposes the insulating properties required of the structure to attain the high crucible temperature in a minimum time with a limited amount of heating power. Therefore, special thermal considerations were given in this area. It was found that the heating rate of the oven is much more sensitive to its conductance to the over-all heat sink of the gas chromatograph package than to the radiation due to its surface emissivity. For this reason, a greater effort was devoted to insulating the oven from the sink than to achieving an exterior surface with a low

emissivity. This problem was solved by insulating the oven from its supports and the oven subassembly mechanisms as near to the oven as possible in order to reduce its effective thermal mass. This insulation was provided by careful selection of structural materials of low conductivity. Through this method, a conductance of only 0.0145 Btu/hr-°F was achieved. As shown by the low heating time and holding power above, the objective of this design has been met.

The thermal design of the column package was restricted by three requirements. The requirements were (1) that the detector block be at a higher temperature than the column coil assembly, (2) that a temperature difference no greater than 1°C exist on the coil assembly during the steady-state operation and (3) that the column package be ready to operate in 35 min with 30 w of power when heating from −50 to +105°C. All of these requirements have been met.

V. ENVIRONMENTAL DEVELOPMENT TESTS

During the development of this instrument, several environmental tests of both the mechanical and thermal type were run on components, subassemblies, and the complete package.

In the thermal area, all of the subassemblies were reduced in temperature to that of lunar-night survival (approximately −185°C) and returned to normal operating temperatures with no loss in performance capability. Areas of major concern which passed these tests successfully were the Viton A O-rings, the electronic equipment, the glass-insulated detectors, and the Viton A diaphragms in the pressure regulator. All of the subassemblies passed the upper survival temperature limit, which corresponds with the upper operating temperature limit.

The mechanical environment that is the most severe to the gas chromatograph is the sinusoidal portion of the vibration encountered during launch. Components and subassemblies that passed individual vibration tests at least as severe as the type-approval requirements are the rotary programming switch of the sample valve subassembly, the oven, and the oven subassembly.

An extensive vibration test was run at JPL on a gas chromatograph package consisting of the complete case and structure of the chromatograph and some of the system components. Figure 9 shows the package mounted on the shaker with accelerometers installed. The components not included in this package were simulated by dummy weights. Components included were the oven subassembly, the programming valve subassembly, and the column and detector subassembly. The components represented by the simulated weights were the standard sample container, the helium cylinder, the solenoid valve and pressure regulator subassembly, and the two electronics H-frames. This package was vibrated along the pitch, roll, and yaw axes to the required vibration of 42 *g* peak-to-peak over a frequency sweep of 20 to 1,500 cps. The test was so severe that seven accelerometers were vibrated off during the three sweeps. The results of the test showed that the over-all structural integrity of the gas chromatograph was satisfactory, except that added stiffening was needed in the cross panel. The stiffening was provided by a perpendicular partition (Fig. 3) with a curved cutout to provide room for the helium container.

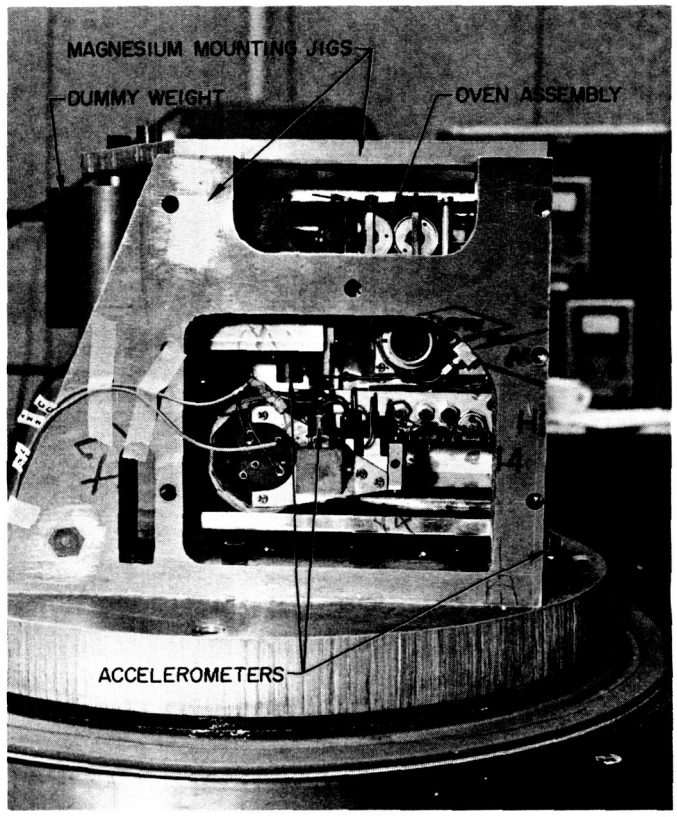

Fig. 9. Developmental model of gas chromatograph, *mounted on shaker*

The philosophy of design of the gas chromatograph is to provide a rigid structure with an over-all resonance frequency in the neighborhood of 500 cps. With this in mind, all subassemblies are mounted rigidly between the top and bottom panels of the instrument or to a cross-panel which is perpendicular to the top and bottom panels. Both the top and bottom panels and the cross panel are made from ⅜-in.-thick honeycomb aluminum sandwiched between aluminum facing sheets. Inserts are provided in the honeycomb at places where various structures and subassemblies are fastened.

The results of the development tests that have been run on the various components and subassemblies and on the entire gas chromatograph package have provided a high degree of confidence in the ability of the gas chromatograph to pass the type-approval tests which will be run in the near future.

VI. FUTURE EVALUATION OF PROTOTYPE MODEL P-2

Prototype model P-2 of the *Surveyor* gas chromatograph will now undergo an extensive evaluation at JPL. One of the main purposes of the evaluation will be to obtain improvement in performance. Also to be evaluated will be the expected life of the various components within the chromatograph, especially the column material.

To aid in this evaluation program, JPL has built a vacuum system as shown in Fig. 10 and a test console made up of four test racks as shown in Fig. 11. The vacuum system is capable of reaching a vacuum of 10^{-7} mm Hg, and with its temperature control facilities can provide a thermal environment from -300 to $+300°F$, controllable within $\pm 10°F$. The test console for the gas chromatograph simulates as nearly as possible the interface between the gas chromatograph and the spacecraft and should provide useful information in the operation of the instrument.

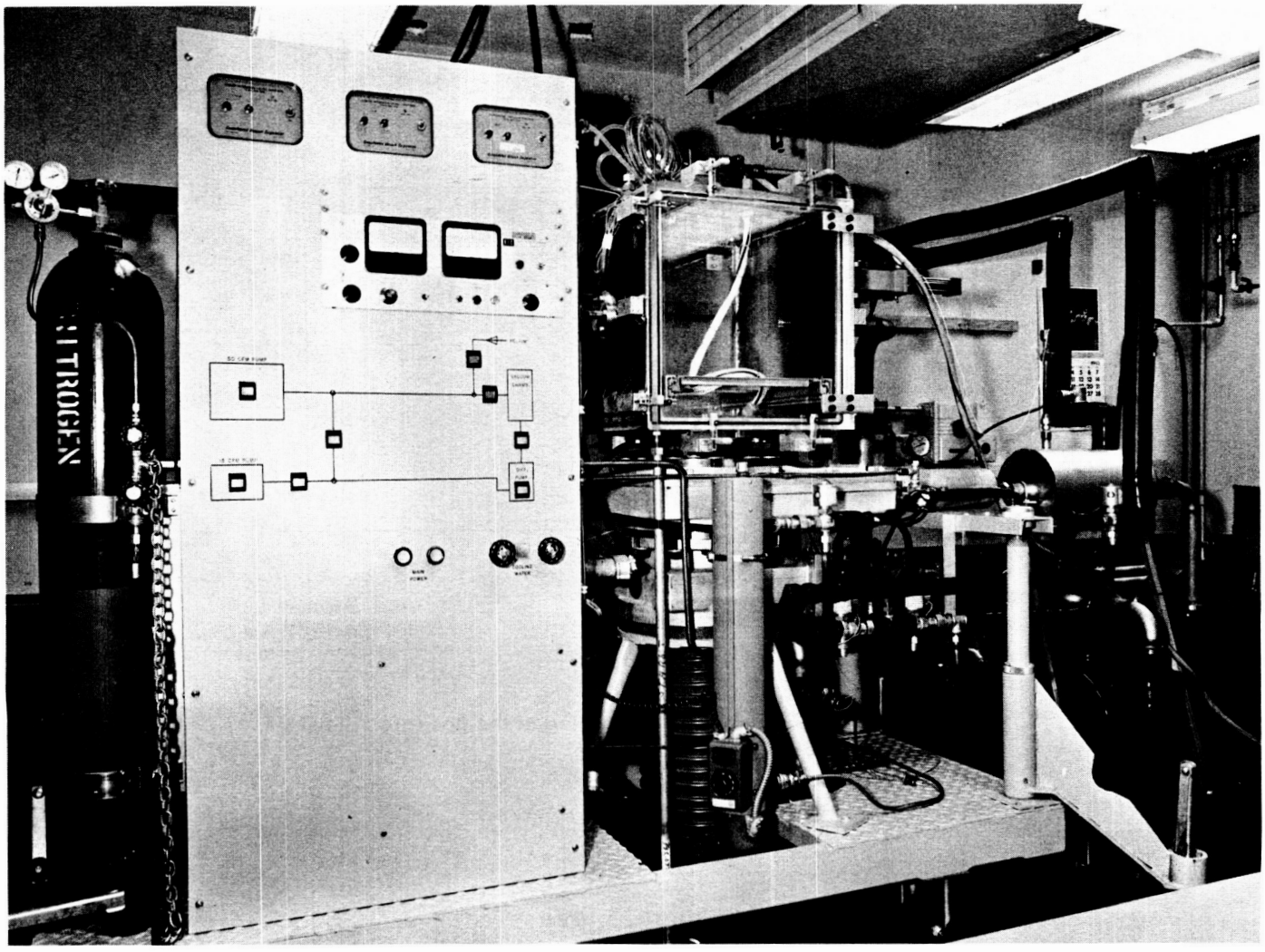

Fig. 10. Vacuum system for evaluation testing of the gas chromatograph

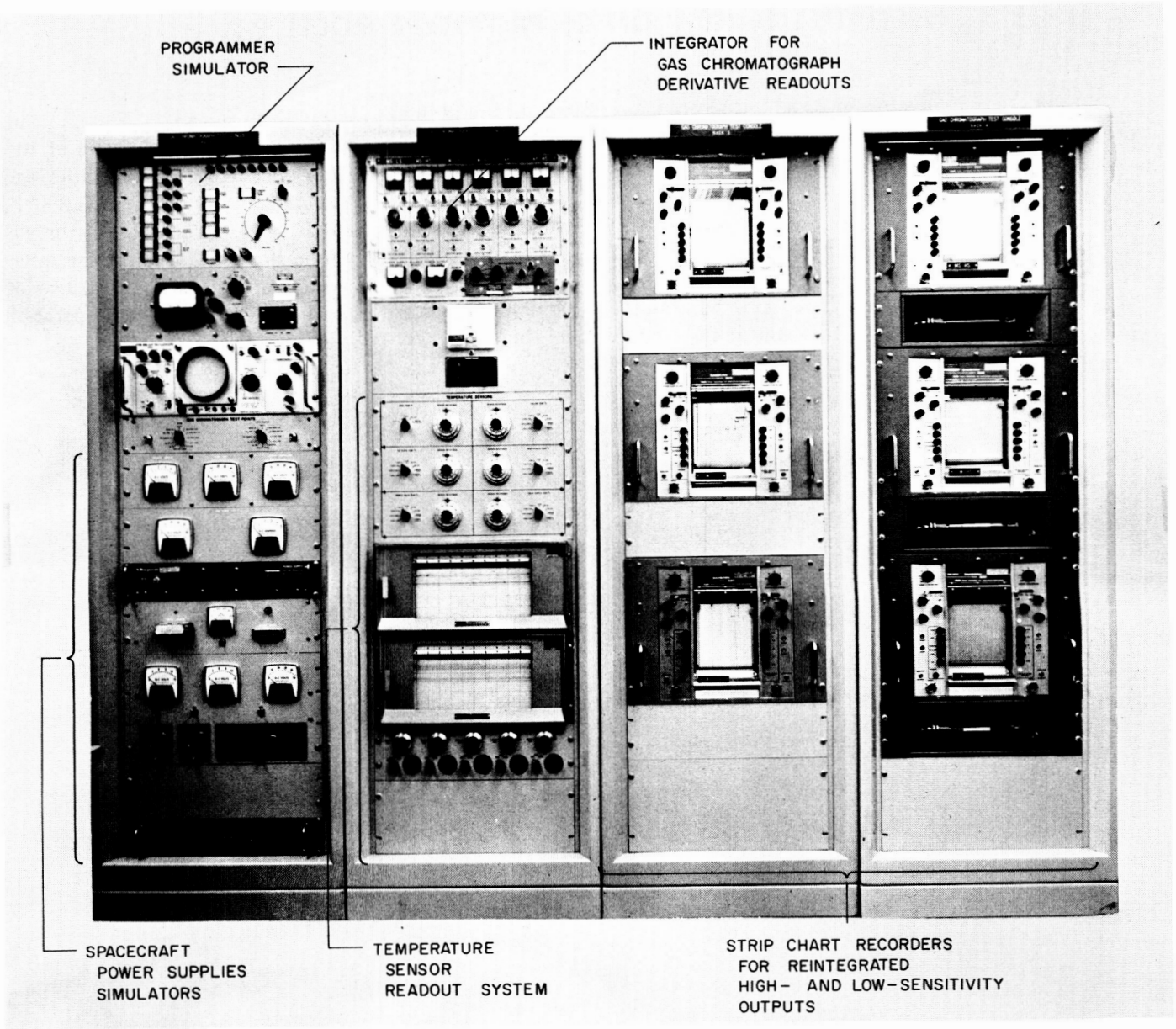

Fig. 11. Test console for evaluation testing of the gas chromatograph

REFERENCES

1. Oyama, V. I., Vango, S. P., and Wilson, E. M., *Applications of Gas Chromatography to the Analyses of Organics, Water, and Adsorbed Gases in the Lunar Crust,* Technical Report No. 32-107, Jet Propulsion Laboratory, Pasadena, California, April 25, 1961.

2. *Design Specification, Surveyor Prototype Equipment, Scientific Instrument,* Specification No. 30851E, Jet Propulsion Laboratory, Pasadena, California, April 16, 1962.

3. *Functional Specification, Surveyor Scientific Instruments, Lunar Gas Chromatograph,* Specification No. S42/43-4-215B, Jet Propulsion Laboratory, Pasadena, California, April 25, 1962.